

Registrar of Patents

Complete Specification

(Section 30(1) — Regulation 28)

| | | | | | |
|----|---|------------------------------------|----|------------------------------|---------------------------|
| 21 | 01 | Official application No. 845117 | 22 | Lodging date 04 -07- 1984 | J&K reference AP 23774 |
| 51 | International classification Co 9 d | | | | |
| 71 | Full Name(s) of applicant(s) BASF LACKE + FARBEN AG BASF FARBEN + FASERN AKTIENGESELLSCHAFT RAAM VERANDER NAME CHANGED 1987 -05- 14 | | | | |
| 72 | Full Name(s) of inventor(s) Wolfgang Batzill; Arnold Dobbelsstein; Michael Geist; Günther Ott. | | | | |
| 54 | Title of invention HEAT-HARDENABLE BINDER MIXTURE. | | | | |

July 4, 1983

~~BASF Farben + Lacke Aktiengesellschaft, Hamburg~~

Heat-hardenable binder mixture

5 The invention relates to a heat-hardenable binder mixture based on a hydroxyl-containing organic resin.

 Various chemical reactions have been proposed, and are indeed used, for hardening the binders in paint films by crosslinking. The chemical bonds formed in the
10 course of the crosslinking reaction frequently do not meet all requirements which are put on paint films.

 In 2-component systems, it is frequently necessary to block one of the reactive groups in order to prevent premature reaction. The compounds then liberated
15 in the course of baking, in particular amines and phenols, are environmental pollutants.

 Electropainting has become widely established in recent years for priming electrically conductive substrates. To date, anodic electropriming has been the
20 focus of interest. The resin binders used for this purpose belong to the carboxyl-containing resins, for example to the maleate oils, maleated epoxy resins, alkyd resins, acrylic resins and in particular the maleated polybutadienes. These resins were water-solubilized by
25 salt formation, predominantly with amines, and were electrodeposited in the electrocoating bath at the anode. However, anodic electropriming has serious disadvantages. For instance, oxygen is evolved at the anode in the

course of the electrodeposition and can have a serious, unfavorable effect on the resins being deposited at the anode. Furthermore, metal ions go into solution at the anode and can end up in the baked film as flaws. The metal ions can lead to discoloration and spotting. They are responsible for qualitative disadvantages by in particular salt formation and hence by reducing the resistance to water and the resistance to corrosion.

The cathodic electropriming process developed to the point of commercial maturity in recent years is increasingly replacing the anodic process, since the defects described above are largely avoided. For instance, the gas evolved at the cathode during the deposition process of the paint film, now at the cathode, is hydrogen, which does not affect the resin binder. Since the cathodic deposition process can take place at approximately neutral pH, hardly any metal ions go into solution. The binders suitable for cathodic deposition predominantly contain amino groups which are water-solubilized by neutralizing them with acids.

European Patent 12,463 B 1 discloses binders which crosslink with hydroxyl-containing resinous compounds by transesterification of β -hydroxyalkylester-containing crosslinking agents. However, this transesterification requires large amounts of heavy metal salts as hardening catalysts.

German Patent 2,934,485 described heat-hardenable binder mixtures which contain Michael adducts as crosslinking agents. The Michael adducts claimed there are

thermally labile adducts of secondary or primary amines on activated double bonds, from which the activated double bonds are released again under hardening conditions and in turn effect, by subsequent Michael addition to the reactive amino groups of an admixed polyamine resin, the hardening of the surface coating composition. In other words, what takes place is a Michael exchange where the primary or secondary amines originally used for blocking the activated double bonds, depending on their volatility, either remain in the free form in the film as basic flaws or are emitted and hence pollute the environment.

It is the object of the invention to avoid these disadvantages of the state of the art and to provide a binder mixture with which surface coating agents can be prepared and whose components are of raised reactivity. The binder mixture of the invention shall help to reduce the environmental pollution during the application of the corresponding surface coating agents. The surface coating agents based on the binder mixture of the invention, furthermore, shall be suitable for all types of application processes, ie. the binder mixture shall be usable for baking finishes to be applied conventionally, for powder finishes, and for aqueous powder slurries. Following the incorporation of solubilizing groups the binder mixture shall be suitable for the electropainting process.

This object is achieved according to the invention for a binder mixture of the type mentioned at the outset when it contains

- A) an organic resin having a hydroxyl group content of at least 0.2 equivalent in 100 g of resin and
- B) a crosslinking agent based on Michael adducts of CH-acidic enolizable carboxylic acid esters on organic materials having α, β -ethylenically unsaturated molecular moieties conjugated with a carbonyl group or a carbonyl group analog.

The binder mixture, in addition to components A and B, advantageously only contains, as component C, pigments, fillers, crosslinking catalysts, corrosion inhibitors and further paint assistants.

Advantageously the proportion of component A is 50 - 95% by weight and that of component B 5 - 50% by weight, the proportions of components A and B adding up to 100%.

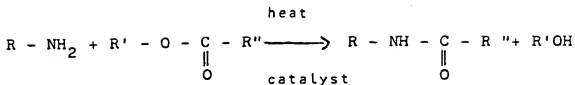
On baking, the binder mixtures according to the invention produce smooth glossy films which are very highly resistant to solvents and which confer excellent corrosion protection on iron metal substrates on which they are coated.

While German Patent 2,934,485, in describing adducts of primary or secondary amines on activated double bonds, debates the thermally reversible cleavage of these β -alanine derivatives and prescribes, as absolutely necessary for the crosslinking reaction, amino groups in the second resin component which are capable of Michael reactions, the existence of hydroxyl groups in the second resin component alone is sufficient in the case of the Michael-adduct-containing crosslinking

agents described in the present invention to ensure excellent resistance to solvents.

Likewise the conventional Michael addition in the form of a nucleophilic addition of compounds having
5 active methylene groups onto activated carbon-carbon double bonds, as used for building the crosslinking agents of the present invention, is referred to in the technical literature (see E.D. Bergmann et al., The Michael Reaction, Org. Reactions 10, 179 et seq. (1959) and
10 Methodicum Chemicum, Volume 5, pages 671 et seq. (1975)) as an equilibrium reaction. In this case, any hardening reaction could be explained by the fact that the CH-acidic carboxylic acid ester is substituted by a hydroxyl group of the second resin component. The CH-acidic carboxylic
15 acid ester in turn is of low volatility, owing to its polar groupings, and as such already is an activated ester which would be bonded to the resin via a trans-esterification reaction.

European Patent 4090 in turn describes synthetic resin binders for cathodic electrocoating which contain
20 crosslinking agents with terminal carboxyl groups of which the majority is esterified with low molecular weight alcohols. This prior art likewise prescribes, in the second resin component, primary or secondary amino groups which are reactive towards the esterified carboxyl
25 groups of the first component, leading to the formation of non-basic amide groups according to the reaction equation:



If the crosslinking agents of the present invention, prepared by way of Michael adduct formation, were thermally stable, only the terminal ester groupings of the crosslinking agent would likewise be responsible for the hardening. Surprisingly, it follows from the present invention that it is merely necessary to have a sufficient number of reactive hydroxyl groups in the second resin component in order to obtain solvent-resistant baked films.

Thus, Michael adduct formation of CH-acidic carboxylic acid esters on activated double bonds likewise activated by electron-withdrawing substituents makes it possible to prepare crosslinking agents which, compared with hydroxyl-containing resins, have a particularly strongly marked crosslinking activity.

The state of affairs according to the invention is also surprising in view of European Patent 12,463 B 1. The binders described there produce their hardening effect by transesterifying crosslinking agents containing β -hydroxyalkylester groups with hydroxyl-containing resins. Activation of the ester groups by a 2-hydroxy substituent in the alcohol moiety is prescribed as absolutely necessary for the ester-containing crosslinking agents named there.

Component A of the binder mixture advantageously has a number average molecular weight of 850 to 20,000, preferably 1,000 to 10,000. In particular, if the binder

mixture is used for electropainting, component A contains primary and/or secondary amino groups in addition to the hydroxyl groups. Tertiary amino groups and quarternary ammonium groups may also be present in addition.

5 The presence of small amounts of primary or secondary amino groups, in addition to the hydroxyl groups in component A, is of importance from the aspect of the solubilization of the resin in aqueous electro-coating baths, since their more strongly marked basicity
10 ensures that the cationic binder dispersions have a longer shelf life.

Binder mixtures whose component A, in addition to hydroxyl groups, also contains primary and/or secondary amino groups are thus a particularly advantageous embodi-
15 ment of the invention.

To prepare component A, primary and/or secondary amino groups are preferably introduced into the organic resin by reacting a polyamine and/or an amino- and/or hydroxyl-containing ketimine with resins which contain
20 at least one, preferably two, epoxy groups or isocyanate groups per molecule.

However, component A can also be obtained by other addition reactions, for example by esterifying or amidating compounds carrying primary and/or secondary
25 amino groups with resins containing groups suitable for this purpose.

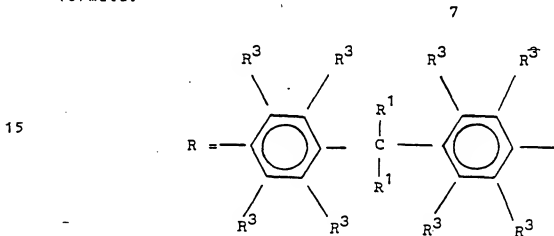
It has been found to be particularly advantageous to prepare component A with epoxy-containing resins having preferably terminal epoxy groups and being selected

from the group consisting of polyglycidyl ethers, polyglycidyl esters and polyglycidylamines.

Other advantageously suitable epoxy-containing resins can be copolymers of acrylic acid and/or methacrylic acid glycidyl esters or of any other olefinically unsaturated, polymerizable compound bearing a glycidyl group with alkyl and/or hydroxyalkyl esters of acrylic and/or methacrylic acid and/or vinyl compounds such as styrene, vinyl toluene or vinyl carbazole.

Partially epoxidized polybutadiene oils are a further particularly suitable group of resins.

For the purposes of this invention polyglycidyl ethers are preferably polyglycidyl ethers of the general formula:



$R^1 = H \text{ or } C_nH_{2n+1}$

$R^2 = (CR^2_2)_n$

$R^3 = R^1, \text{ halogen or preferably H}$

$n = 0 \text{ to } 5.$

20 The polyglycidyl ethers of the general formula shown above have a number average molecular weight of about 340 to 5,000 and correspondingly an epoxy equivalent weight of 170 to 2,500. The epoxy resins can also be

used in the hydrogenated or partially hydrogenated form. To control the film properties, a portion of the reactive groups of the epoxy resin can be reacted with other compounds. Suitable for this purpose are:

- 5 a) carboxyl-containing compounds such as saturated or unsaturated monocarboxylic acids (for example benzoic acid, linoleic acid, 2-ethylhexanoic acid, Versatic acid), aliphatic, cycloaliphatic and/or aromatic dicarboxylic acids of various chain lengths (for example 10 adipic acid, sebacic acid, isophthalic acid or dimeric fatty acids), hydroxyalkylcarboxylic acids (for example lactic acid, dimethylolpropionic acid) and carboxyl-containing polyesters or
- 15 b) amino-containing compounds such as diethylamine or ethylhexylamine or diamines having secondary amino groups, such as, for example, N,N'-dialkylalkylenediamine such as dimethylethylenediamine, N,N'-dialkylpolyoxyalkylenediamine such as N,N'-dimethylpolyoxypropylenediamine, polyaminoamides such as Versamides 20 with two moles of monoglycidyl ethers or monoglycidyl esters, especially glycidyl esters of α -branched fatty acids such as Versatic acid or
- c) hydroxyl-containing compounds such as neopentyl glycol, bis-ethoxylated neopentyl glycol, neopentyl glycol 25 hydroxypivalate, hexane-1,6-diol, hexane-2,5-diol, 1,4-bis-(hydroxymethyl)-cyclohexane, 1,1-isopropylidene-bis-(p-phenoxy)-2-propanol, trimethylolpropane, pentaerythritol or amino alcohols such as triethanolamine, methyldiethanolamine or hydroxyl-containing

alkylketimines such as aminomethylpropane-1,3-diol
methyl isobutyl ketimine and also polyglycol ethers,
polyester-polyols, polyether-polyols, polycaprolactone-
polyols of different functionalities and molecular
5 weights.

Instead of using polyglycidal ethers based on
bisphenol A it is also possible to use polyglycidyl ethers
based on other components such as triglycidyl isocyanur-
ate, etherocyclic diglycidyl compounds or diglycidylhydant-
10 toins.

Examples of suitable polyglycidyl esters are reac-
tion products of, for example, bisglycidyl terephthalic or
glycidyl isophthalic acid with, for example, bisphenol A.
The epoxy equivalent weight of these products is between
15 200 and 2,500. To control the film properties, a portion
of the remaining reactive glycidyl groups can be reacted
with other compounds. Suitable for this purpose are the
compounds mentioned above under a, b and c.

For the purposes of this invention polyglycidyl-
20 amines are glycidyl-containing resins which are obtained
by introducing glycidyl groups into NH_2 -functional resins
via, for example, epichlorohydrin.

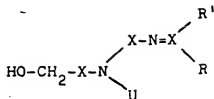
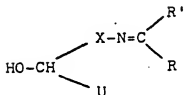
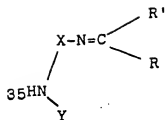
Also particularly suitable are copolymers of
acrylic and/or methacrylic acid glycidyl esters or of any
25 other olefinically unsaturated polymerizable compound
bearing a glycidyl group with esters of acrylic and/or
methacrylic acid as well as polymerizable vinyl compounds
which have a number average molecular weight of 700 to
10,000 and an epoxy equivalent weight of 600 to 3,000.

Preference goes to acrylic acid esters with C₂- to C₈- alcohols and methacrylic acid esters with C₁- to C₄- alcohols. The copolymers can contain further monomers such as hydroxyalkyl (meth)acrylate or (meth)acrylamide.

5 The copolymerization is effected in well known manner by solution, suspension or emulsion polymerization in the presence of free-radical initiators such as peroxides, hydroperoxides, per-esters or thermolabile azo compounds, and, if desired, of molecular weight regulators.

10 For the purposes of the present invention, partially epoxidized polybutadiene oils are reaction products obtained by reacting commercially available polybutadiene oils with per-acids or organic acid/H₂O₂ mixtures. The method of preparation is described in, for
15 example, Chemiker-Zeitung 95, 857 et seq. (1971).

 To prepare water-dispersible binders, the epoxy-containing resins are reacted with polyamines and/or an amino- and/or hydroxyl-containing ketimine. If the addition reaction of the compounds bearing primary and
20 secondary amino groups is carried out in the form of their ketimines, the reaction conditions must be controlled in such a way that no ketimine-decomposing substances remain in the reaction product. The preferred ketimines are reaction products of ketones and such alkylamines or
25 alkyldiamines as contain hydroxyl or secondary amino groups and have the general structures R-NH-R-NH₂ and HO-R-NH₂ respectively. The ketimines have for example the following structures:



where

X = $-(\text{CR}_2)_n-$

5 R = -H, -R',

R' = $-\text{C}_m\text{H}_{2m+1}$, $-\text{C}_6\text{H}_{11}$

U = -R, -Y

Y = $-\text{X}-\text{N}=\begin{array}{c} \text{R}' \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R} \end{array}$, -X-OH, -R' or $-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{O}-\text{Z}-\text{R}'$

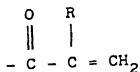
Z = $=\text{CO}$, -X

10 n = 1 - 6

m = 1 - 12.

The ketones used for the reaction with the primary amino groups are generally aliphatic ketones such as methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone or ethyl n-propyl ketone and cycloaliphatic ketones such as cyclopentanone and cyclohexanone. The preferred aminoalkylamines and alkanolamines are in the main diethylene-triamines, N-methylethylenediamine, N-methylpropylenediamine, N-aminoethylpiperazine, 2-aminoethanol, 1-amino-

Examples thereof are polyfunctional acrylates or methacrylates having at least two groups of the formula



in which R is hydrogen or a lower alkyl radical, for example a methyl or ethyl radical. The preceding formula is attached to an organic radical which can be an alkyl, aryl, alkaryl or a polymeric radical.

The preferred polyfunctional acrylates and methacrylates, ie. compounds containing 2 or more acrylate and methacrylate groups respectively, are obtained by reacting organic polyols with acrylic or methacrylic acid. Examples of suitable compounds of this type are ethylene glycol diacrylate, 1,4-butanediol dimethacrylate, bisphenol A diacrylate, diethylene glycol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, trimethylolpropane triacrylate, bisphenol A dimethacrylate, polyethylene glycol dimethacrylate and 1,6-hexanediol diacrylate.

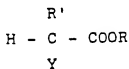
Suitable organic materials, in addition to polyfunctional acrylates and methacrylates, are the following compounds:

1. reaction products of polyisocyanates, preferably diisocyanates, such as toluene diisocyanate, or prepolymerized terminal isocyanate groups, with hydroxyl-containing acrylates or methacrylates, such as 2-hydroxyethyl acrylate or hydroxypropyl methacrylate;
2. transesterification products of polymeric polyols, such

as hydroxyl-containing acrylic resins, polyester-polyols, including polyesters derived from lactones, and polyether-polyols, with N-alkoxymethylacrylamides and N-alkoxymethacrylamides;

- 5 3. reaction products of epoxy-containing resinous materials with acrylic or methacrylic acid. The CH-acidic enolizable carboxylic acid esters can also be added on to high molecular weight compounds having unsaturated molecular moieties activated by a carbonyl group, such as, for example, unsaturated polyesters based on maleic acid, fumaric acid, itaconic acid or similar acids.

The carboxylic acid esters which are made to react with the organic material which contains α, β -ethylenically unsaturated molecular moieties conjugated with carbonyl groups or carbonyl group analogs can be represented in schematic form by the formula



where R is an alkyl or alkoxy radical, R' is hydrogen, an alkyl or aryl radical or an acetamino group, and Y is an electron-attracting group of the type -CO-R, -COOR, -CN-CO-NH-R or -(CR'R'')_n-COOR where n can be 0 to 2.

Selected examples from the said class of CH-activated carboxylic acid esters are ethyl cyanacetate, ethyl acetoacetate, ethyl isopropylacetoacetate, ethyl cyclohexanone-2-carboxylate, diethyl malonate, dipropyl malonate, diethyl butylmalonate, diethyl acetaminomaltonate

and 2-ethoxyethyl acetoacetate.

The crosslinking agent (B) can advantageously be prepared as follows. To start with, the carboxylic acid ester component described above is introduced first, and
5 a catalyst is added to it. Numerous basic substances can be used as the catalyst. Examples are alkali metal hydroxides or alcoholates, pyridine and sodium amide. The material containing activated CC double bonds, if desired in the form of an inert dilution, is gradually added dropwise.
10 In many cases, an exothermic reaction sets in even at room temperature and can be kept under control by the rate of the dropwise addition. In some cases it can also be necessary to cool the reaction mixture. After the addition the reaction mixture is stirred until it contains
15 no detectable double bonds or until the viscosity of the product remains constant.

In the case of less reactive systems the reaction temperature can be raised, but it is best kept below 80°C in order to prevent basic decomposition of the
20 components. In the case of more strongly CH-acidic carboxylic acid esters, for example β -ketocarboxylic acid esters, which give rise to spontaneous enolization, there is in turn no need for any catalysis.

Some of the said carboxylic acid esters possess
25 two active hydrogen atoms, so that addition can take place onto two activated CC double bonds, leading to a longer chain for the crosslinking agent. It is accordingly possible to control desired molecular weights by choosing suitable stoichiometric ratios.

The binder mixture according to the invention can be in finely divided solid form or in the form of a solution in an organic solvent.

For the electrocoating process it is necessary that, after protonation with acid, the binder mixture is in the form of an aqueous solution or dispersion.

The binder component and/or crosslinking component is water-solubilized by neutralizing, with acids, the primary, secondary and/or tertiary amino groups they contain. Suitable acids are in particular organic acids, but it is also possible to use, for example, hydrochloric acid or phosphoric acid. The amino groups are preferably neutralized with formic acid, acetic acid, malonic acid or citric acid.

Said acids can also be used when the solubilizing groups for the binder component and/or crosslinking component are introduced by addition of an ammonium group or the salt of a sulfide/acid or phosphine/acid mixture onto the binder or the crosslinking agent.

The degree of neutralization of the solubilizing groups, based on these groups, is between 0.2 and 1.0 equivalent and preferably between 0.25 and 0.6 equivalent of acid.

The neutralization can be carried out as follows. The acid is introduced into water, if desired together with dispersing auxiliaries, and the resin solution is stirred into the water at room temperature or if necessary at elevated temperatures. However, the acid can also be added directly to the resin solution. The neutralized

resin solution can then be stirred into the water, but, if desired, the water can also be slowly incorporated into the resin solution. To control its viscosity, the deposition voltage and the flow properties, the dispersion can contain up to 20% of organic solvent. If, as a result of the chosen method of preparation, the made-up batch contains too much solvent or even solvents having an adverse effect on the properties, they can be distilled out of the resin solution before it is dispersed or they are distilled out of the aqueous dispersion. It is advantageous for the properties as a whole if the organic solvent content is as low as possible.

The solids content of a deposition bath made up with the dispersion according to the invention is 7-35% by weight, but preferably 12-25% by weight. The deposition bath is at pH 4 - 8, but preferably pH 5 - 7.5. The anodes of the deposition bath are made of non-corroding steel or graphite. The temperature of the made-up bath shall be between 15 and 35°C, preferably between 20 and 30°C. The deposition time and voltage are chosen to be such that the desired film thickness is obtained.

After the paint film has been deposited the coated article is rinsed and is ready for baking.

Irrespective of the method used to apply the coating agent based on the binder mixture according to the invention, the paint film is crosslinked in the course of baking at temperatures of 130 to 200°C for 10-60 minutes, preferably at 150 to 180°C for 15-30 minutes.

The crosslinking reaction can be speeded up still

more by means of suitable catalysts. Suitable for this purpose are in particular ammonium compounds such as benzyltrimethylammonium hydroxide, benzyltrimethylammonium chloride, trimethylcetyl ammonium bromide and tetraammonium iodide and organic tin compounds such as dibutyltin dilaurate and iron(III) acetylacetonate, zinc acetate, zinc 2-ethylhexoate, cobalt naphthenate, lead acetate, lead octoate and butyl titanate. Owing to the high reactivity of the binder components the crosslinking reaction is soon speeded up by small amounts of catalysts.

The pigmentation is effected in a well known manner by milling the pigments and the customary additives, such as fillers, corrosion inhibitors and antifoams (component C) in one of the two binder components. The milling apparatus can be for example sand mills, ball mills or three-roll mills. The paint can then be completed in the generally known manner.

The individual components A and B and if present component C can be mixed in their concentrated solutions and be dispersed together. However, it is also possible to disperse components A and B individually - their pigments being milled in either A or B - and to mix the dispersion of the individual components in the required ratio.

The invention further relates to a process for preparing surface coatings by applying a coating agent to a substrate in the form of a film by baking, the coating agent containing a binder mixture which contains the mixture

- A) an organic resin having a hydroxyl group content of at least 0.2 equivalent in 100 g of resin and
- B) a crosslinking agent based on Michael adducts of CH-acidic enolizable carboxylic acid esters on organic materials having α, β -ethylenically unsaturated molecular moieties conjugated with a carbonyl group or a carbonyl group analog.

Advantageous embodiments of the process according to the invention are given by subclaims 12 to 21.

- 10 The invention further relates to the use, in the preparation of such coatings, of a binder mixture which contains the mixture

- A) an organic resin having a hydroxyl group content of at least 0.2 equivalent in 100 g of resin and
- 15 B) a crosslinking agent based on Michael adducts of CH-acidic enolizable carboxylic acid esters on organic materials having α, β -ethylenically unsaturated molecular moieties conjugated with a carbonyl group or a carbonyl group analog.

- 20 Advantageous embodiments of the use according to the invention are given by subclaims 22 to 33.

Below, the invention is illustrated in more detail by means of illustrative embodiments.

Example 1:

- 25 Preparation of a crosslinking agent (Crosslinking agent I)

288 g of diethyl malonate and 19 g of ethanolic sodium ethanolate solution (3.8% by weight of sodium) are introduced into a reaction vessel equipped with a stirrer, nitrogen inlet, reflux condenser, dropping funnel

- and internal thermometer and are heated to 38°C. 226 g of 1,6-hexanediol diacrylate are added dropwise in such a way, with occasional slight cooling, that the internal temperature does not exceed 40°C. The mixture is then
- 5 stirred at 40°C until the viscosity is constant, which takes about 4 hours. The result is a clear, colorless product having an original viscosity of 450 mPas (25°C).

Example 2:

Preparation of a crosslinking agent (Crosslinking agent II)

- 10 Crosslinking agent II is obtained analogously to Example 1 from 417 g of diethyl malonate, 26 g of ethanolic sodium ethanolate solution and 296 g of trimethylolpropane triacrylate.

Example 3:

- 15 Preparation of a crosslinking agent (Crosslinking agent III)

Precursor A:

- 468 g of acrylic acid and 1,700 g of glycidyl Versatate are carefully heated to 90°C in a 4 liter reaction vessel equipped with a stirrer, inert gas supply,
- 20 reflux condenser and internal thermometer in the presence of 10 g of a chromium catalyst and of 1 g of hydroquinone. After the slightly exothermic reaction has died down this temperature is maintained further until the acid number is less than 1 mg of KOH/g.

- 25 Crosslinking agent III:

2,011 g of the above precursor A are added dropwise by way of a dropping funnel, analogously to Example 1, to a mixture of 880 g of diethyl malonate and 87 g of sodium ethanolate solution and the mixture reacts to

produce crosslinking agent III.

Example 4:

Preparation of a crosslinking agent (Crosslinking agent IV)

- 5 Crosslinking agent IV is obtained analogously to
Example 1 from 338 g of ethyl acetoacetate and 296 g of
trimethylolpropane triacrylate, the reaction being cata-
lyzed by 19 g of sodium ethanolate solution.

Example 5:

Preparation of hydroxyl-containing resins

10 Resin I:

- 1,786 g of a commercially available bisphenol A
epoxy resin having an epoxy equivalent weight of 839,
62 g of xylene and 273 g of methyl isobutyl ketone are
heated to 80°C in a 4-liter reactor equipped with a
15 stirrer, attached reflux condenser, internal thermometer
and inert gas line. When the contents have been homo-
genized, 208 g of diethanolamine are added with stirring,
during which addition the internal temperature rises to
110°C. After the exothermic reaction has died down
20 the reaction mixture is held at 105°C until the epoxy
equivalent weight has reached an infinite value, which
takes about 2 hours. The reaction product is then brought
to a solids content of 80% with 163 g of hexylglycol, is
cooled, and is discharged.

- 25 Viscosity (25°C): 380 mPas (50% strength in
ethylglycol)

MEQ base: 1.0 milliequivalents/g.

Resin II

In a reactor as described above, 1,944 g of a

commercially available bisphenol A epoxy resin having an epoxy equivalent weight of 486 is turned into a melt a little at a time at 110°C, 557 g of methyl isobutyl ketone are added, and the mixture is stripped of water by azeotropic distillation at 120°C for 20 minutes. After the mixture has cooled down to 60°C, 139 g of hexylglycol are added and 210 g of diethanolamine are gradually added dropwise.

The reaction mixture is held at this temperature until the total of epoxy content and amine content has reached 1.9 milliequivalents/g.

630 g of an adduct of 1 mole of hexamethylenediamine and 2 moles of glycidyl Versatate are then added, and the temperature is raised to 120°C in the course of 1 hour. This temperature is maintained until the total value of epoxy and amine content has reached 1.5 milliequivalents/g, and the mixture is cooled down and discharged.

Viscosity (23°): 470 dPas (50% strength in ethylglycol)

MEQ base: 1.5 milliequivalents/g

Solids content (1 hour at 130°C): 83%

Resin having hydroxyl groups and primary amino groups (Resin III):

In a reactor as described above, 1,770 g of a commercially available bisphenol A epoxy resin having an epoxy equivalent weight of 885 are melted at 100°C in the presence of 62 g of xylene. The melt is diluted with 219 g of methyl isobutyl ketone, and the residual water is distilled out under a slight vacuum in the course of

15 minutes. 153 g of an adduct of 1 mole of diethylene-
triamine and 2 moles of methyl isobutyl ketone (70% strength
in methyl isobutyl ketone) and 118 g of methylethanolamine
are added in succession with slight cooling, whereupon
5 the temperature rises to 110°C. This temperature is
maintained for a further 2 hours, and the mixture is then
diluted with 160 g of hexylglycol.

Viscosity (25°C): 590 mPas (50% strength in
ethylglycol)

10 MEQ base: 1.4 milliequivalents/g

Solids content: 82% (1 hour at 130°C)

Example 6:

Preparation of high-solids organically dissolved clear
finishes and their hardening under heat.

15 Resins I, II and III of Example 5 were mixed with
the crosslinking agents (Crosslinking agents I-VI) of
Examples 1-4 in the weight ratios given in the table, and
homogenized. The mixtures were adjusted to a solids con-
tent of 50% with ethylglycol. 0.5 g of H₂O was addition-
20 ally added in the case of resin III. The clear finishes
thus obtained were catalyzed in some cases, were knife-
coated onto zinc-phosphatized steel sheets (wet film
thickness 50 μ m) and were baked for 20 minutes under the
conditions specified in the table below. The result is
25 in all cases a smooth, glossy film.

Table: Binder mixtures according to Examples 1-5

| Resin (in grams) | Crosslinking agent (in grams) | Catalyst ¹⁾ (in grams) | Baking Conditions ²⁾ | MIBK Test ³⁾ | Bending Test |
|---------------------|----------------------------------|--------------------------------------|---------------------------------|-------------------------|--------------|
| 36.8 I | 16.5 I | 1.3 | 20/180 | 100 | ok |
| 36.8 I | 16.5 II | 1.3 | 20/160 | >100 | ok |
| 36.8 I | 16.5 III | 1.2 | 20/160 | 80 | ok |
| 36.8 I | 16.5 IV | - | 20/180 | >100 | ok |
| 38.6 II | 16.5 IV | 1.5 | 20/180 | >100 | ok |
| 38.6 II | 16.5 II | 1.5 | 20/160 | 100 | ok |
| 38.6 II | 16.5 III | 1.1 | 20/180 | >100 | ok |
| 40.8 III | 16.5 I | 1.0 | 20/160 | 20 | ok |
| 40.8 III | 16.5 IV | 1.5 | 20/180 | >100 | ok |

1) Commercially available lead(II) octoate solution (24% of lead)

2) Time/temperature in minutes/°C

3) Number of forward and backward strokes with a rag soaked in methyl isobutyl ketone until a visible mark has been left on the film.

Example 7:

Preparation of a binder dispersion

A binder mixture is prepared from the following components:

- 5 613 g of resin II (Example 5)
 220 g of crosslinking agent II (Example 2)
 1 g of a surface-active additive
 22 g of lead(II) octoate solution (24% of lead)

The binder mixture is briefly heated to 60°C and
10 is then stirred into a dispersing bath containing 14.2 g
of glacial acetic acid and 618 g of deionized water. The
mixture is homogenized for a further hour before it is
slowly diluted with 628 g of deionized water. The result
is a finely divided dispersion which, when subsequently
freed of solvent under vacuum, has the following parameters:

Solids content (1 hour at 130°C): 33%

MEQ base: 1.27 milliequivalents/g

MEQ acid: 0.38 milliequivalents/g

pH: 6.4

20 Example 8:

Preparation of a gray pigment paste

- 800 parts of butyl glycol are added to 953 parts
of a commercially available epoxy resin based on bis-
phenol A and having an epoxy equivalent weight of 890.
25 The mixture is heated to 80°C. To the resin solution
are then added 221 parts of a reaction product of 101
parts of dimethylethanolamine and 120 parts of 80% strength
aqueous lactic acid. The reaction is carried out at
80°C until the acid number has dropped to below 1.

1,800 parts of this product are initially introduced together with 2,447 parts of deionized water and are mixed with 2,460 parts of TiO_2 , 590 parts of an extender based on aluminum silicate, 135 parts of lead silicate, 37 parts of carbon black and 25 parts of lead octoate. This mixture is comminuted to a Hegman fineness of 5-7 in a milling apparatus. Thereafter, 1,255 parts of deionized water are added in order to obtain the desired paste consistency. This gray paste has a very long shelf life.

Example 9:

Preparation of an electrocoating bath and deposition:

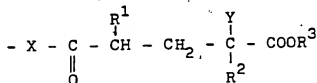
1,805 g of deionized water are added to 1,780 g of the binder dispersion described in Example 9 and 456 g of the pigment paste described in Example 8. The solids content is 18%. The pH is 6.3. Zinc-phosphatized steel sheets were coated at a bath temperature of 25°C for 120 seconds (deposition voltage for 18-20 μm dry film thickness: 280 V), are rinsed with water and are baked at 180°C for 20 minutes. The result is smooth, firmly adhering, solvent-resistant films having the following properties:

| | |
|------------------------|----------------|
| Cross hatch: | 0 |
| Erichsen deep-drawing: | 9 mm |
| Reverse impact: | 80 inch pound |
| Impact: | 80 inch pound. |

What is claimed is:

1. A heat-hardenable binder mixture which contains
 - A) an organic resin having a hydroxyl group content of at least 0.2 equivalent in 100 g of resin and
 - B) a crosslinking agent based on Michael adducts of CH-acidic enolizable carboxylic acid esters on organic materials having α, β -ethylenically unsaturated molecular moieties conjugated with a carbonyl group or a carbonyl group analog.

2. A binder mixture as claimed in claim 1, wherein the crosslinking agent (B) contains structural units of the formula



where

R^1 = H, alkyl or aryl,

R^2 = H, alkyl, aryl or $-CH_2-\overset{\overset{R^1}{|}}{\underset{\underset{O}{||}}{C}}-X-$

R^3 = alkyl, aryl or $-CH_2-CH_2-O-R^4$,

X = O or NH,

Y = $-\overset{\overset{O}{||}}{C}-R^4$, -CN or $-(CR^1_2)_n-COOR^3$

where n = 0 to 11,

R^4 = alkyl or aryl.

3. A binder mixture as claimed in claim 1, which, in addition to components A and B, contains, as component C, pigments, fillers, crosslinking catalysts, corrosion inhibitors and further paint assistants.

4. A binder mixture as claimed in claims 1 to 3, wherein the proportion of component A is 50 - 95% by weight and that of component B 5 - 50% by weight, the proportions of components A and B adding up to 100%.
5. A binder mixture as claimed in claims 1 to 4, wherein component A has a number average molecular weight of 1000 - 20,000.
6. A binder mixture as claimed in claims 1 to 5, wherein component A, in addition to the hydroxyl groups, contains amino groups or ammonium groups.
7. A binder mixture as claimed in claims 1 to 6, wherein component B has a number average molecular weight of 200 - 10,000.
8. A binder mixture as claimed in claims 1 to 7, which is in finely divided solid form.
9. A binder mixture as claimed in claims 1 to 7, which is in the form of a solution in an organic solvent.
10. A binder mixture as claimed in claims 5 to 7, which, following protonation with acid, is in the form of an aqueous solution or dispersion.
11. A process for preparing surface coatings by applying a coating agent to a substrate in the form of a film and then hardening the film by baking, the coating agent containing a binder mixture, wherein the binder mixture contains
 - A) an organic resin having a hydroxyl group content of at least 0.2 equivalent in 100 g of resin and
 - B) a crosslinking agent based on Michael adducts of CH-acidic enolizable carboxylic acid esters on organic

materials having α, β -ethylenically unsaturated molecular moieties conjugated with a carbonyl group or a carbonyl group analog.

12. A process as claimed in claim 11, wherein the mixture, in addition to components A and B, contains as component C pigments, fillers, crosslinking catalysts, corrosion inhibitors and further paint assistants.

13. A process as claimed in claims 11 and 12, wherein the proportion of component A is 50 - 95% by weight and that of component B 5 - 50% by weight, the proportions of components A and B adding up to 100%.

14. A process as claimed in claims 11 to 13, wherein component A has a number average molecular weight of 1,000 - 20,000.

15. A process as claimed in claims 11 to 14, wherein component A, in addition to the hydroxyl groups, contains amino groups or ammonium groups.

16. A process as claimed in claims 11 to 15, wherein component B has a number average molecular weight of 200 - 10,000.

17. A process as claimed in claims 11 to 16, wherein the coating agent is in finely divided solid form.

18. A process as claimed in claim 17, wherein the coating agent is applied by an electrostatic powder spray device.

19. A process as claimed in claims 11 to 16, wherein the binder mixture is in the form of a solution in an organic solvent.

20. A process as claimed in claim 19, wherein the

coating agent is applied by spraying, dipping, flow-coating, roll-coating, knife-coating or the like.

21. A process as claimed in claims 15 and 16, wherein an electrically conductive substrate is dipped into an aqueous bath of the at least partially acid-neutralized coating agent, which may additionally contain organic solvents, and is connected as the cathode, the film is deposited on the substrate by means of direct current, the substrate is removed from the bath, and the film is hardened by baking.

22. The use of a binder mixture for the preparation of surface coatings, wherein the mixture contains

A) an organic resin having a hydroxyl group content of at least 0.2 equivalent in 100 g of resin and

B) a crosslinking agent based on Michael adducts of CH-acidic enolizable carboxylic acid esters on organic materials having α, β -ethylenically unsaturated molecular moieties conjugated with a carbonyl group or a carbonyl group analog.

23. The use as claimed in claim 22, wherein the mixture, in addition to components A and B, contains as component C pigments, fillers, crosslinking catalysts, corrosion inhibitors and further paint assistants.

24. The use as claimed in claims 22 and 23, wherein the proportion of component A is 50 - 95% by weight and that of component B 5 - 50% by weight, the proportions of components A and B adding up to 100%.

25. The use as claimed in claims 22 to 24, wherein component A has a number average molecular weight of

1,000 - 20,000.

26. The use as claimed in claims 22 to 25, wherein component A, in addition to the hydroxyl groups, contains amino groups or ammonium groups.

27. The use as claimed in claims 22 to 26, wherein component B has a number average molecular weight of 200 - 10,000.

28. The use as claimed in claims 22 to 27, wherein the binder mixture is in finely divided, solid form.

29. The use of the binder mixture as claimed in claim 28, for powder finishes.

30. The use according to claims 22 to 27, wherein the binder mixture is in the form of a solution in an organic solvent.

31. The use of the binder mixture as claimed in claim 30, for baking finishes.

32. The use according to claims 26 and 27, wherein the binder mixture, after protonation with acid, is in the form of an aqueous solution or dispersion.

33. The use of the binder mixture as claimed in claim 32, for cathodic electropainting.

- 4 JUL 1984


JOHN AND KERNICK
FOR THE APPLICANTS